LOW TEMPERATURE BEHAVIOR OF N-5 PROPELLANT

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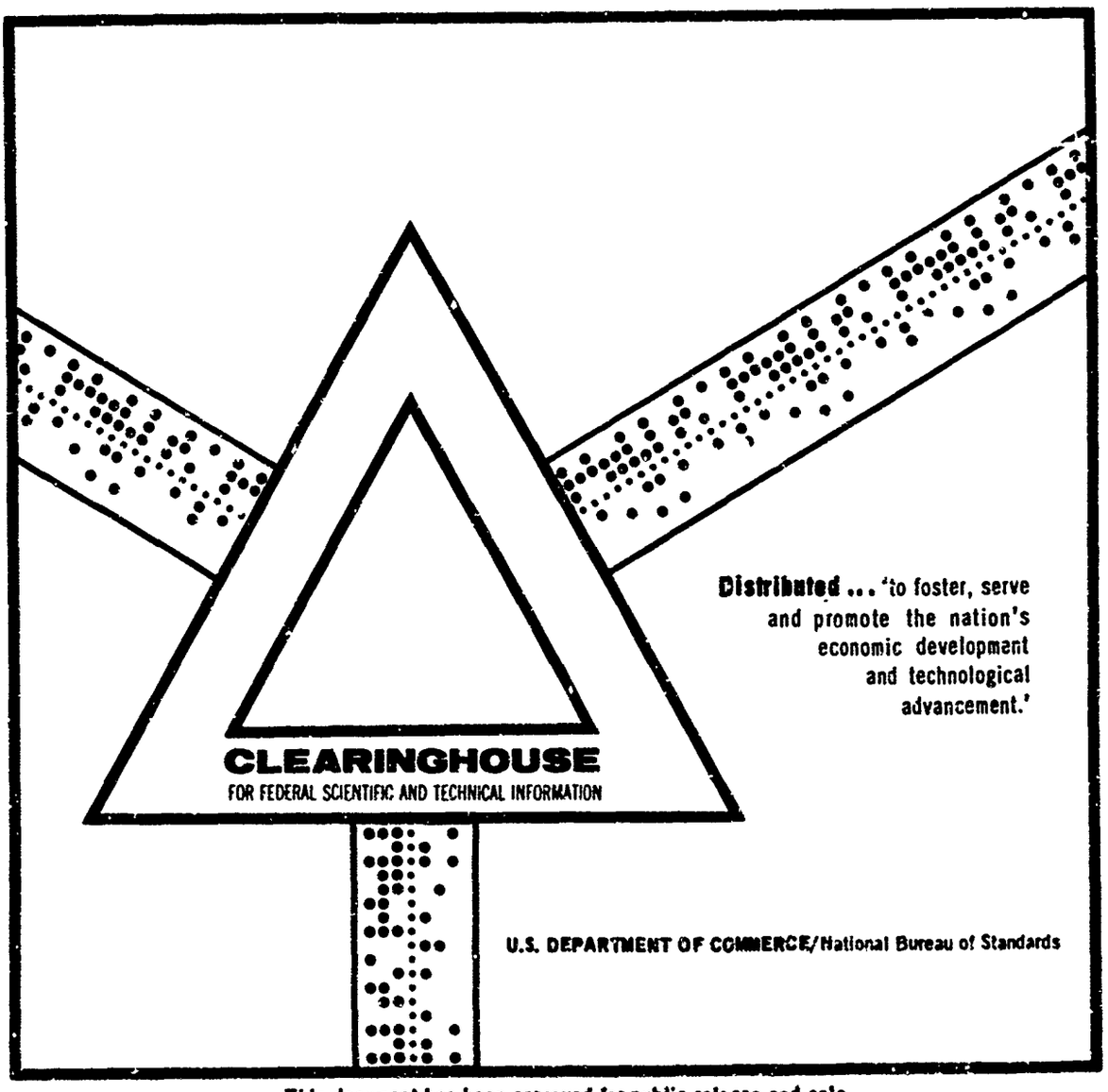
Cold Regions Research and Engineering Laboratory
Hanover, New Hampshire

January 1970



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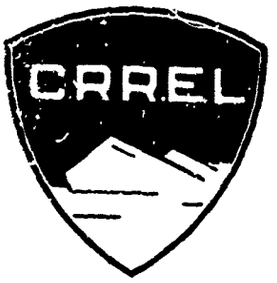

Special Report 142

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Allen Tice
and
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PREFACE

This report was prepared by Dr. Duane M. Anderson, Chief, Earth Sciences Branch; Allen R. Tice, Engineering Technician; and SP 5 Brian A. Bartizek. The authors are members of the Research Division, U.S. Army Cold Regions Research and Engineering Laboratory.

The project was funded by the 2.75 FFAR project manager's office, Picatinny Arsenal, Dover, New Jersey.

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LOW TEMPERATURE BEHAVIOR OF N-5 PROPELLANT

by

Duane M. Anderson, Allen Tice and Brian Bartizek

INTRODUCTION

In response to a request from the 2.75 Folding Fin Aerial Rocket (FFAR) project manager's office, Picatinny Arsenal, Dover, New Jersey, the low temperature behavior of N-5 propellant has been investigated by differential thermal analysis (DTA), dilatometry, and low temperature stress-strain measurements. This work was stimulated by the need to determine the cause of a noticeable increase in the number of malfunctions in static firings and flight tests of 2.75 FFAR motors conditioned at low temperature. Some of the failures were traced to mechanical defects in the rocket motor but others seemed to result from cracks or inhomogeneities in the propellant. An inter-service committee was organized by the 2.75 FFAR project manager's office to investigate these possibilities. Since USA CRREL was conducting a study of the low temperature behavior of some composite solid propellants to determine whether or not low temperature phase separations were common, this laboratory was asked to investigate the possibility of propellant defects.

N-5 is a propellant formula developed by the U.S. Navy. Before the Viet Nam conflict it was only briefly used and for some years it has been considered more or less obsolete. For this reason its physical and mechanical properties have never been thoroughly determined.

The present study was designed to achieve the following objectives:

1. To determine whether or not phase changes attributable to such phenomena as sequential freezing of one or more components, demixing of components, or a change in state of one or more components occur as N-5 propellant is cooled to -65°F (-53.9°C) and below.*

2. To determine the "glass transition temperature," the coefficients of thermal expansion, and the significant stress-strain relationships required for grain structural analysis of N-5 propellant.

3. To determine the magnitude of plant-to-plant variations and within-plant variations in physical properties of propellant grains produced at the three currently active production plants.

PRIOR WORK

Differential thermal analysis (DTA) is a technique useful in locating phase transition temperatures in a substance or material as it is heated or cooled. Chemical recombinations, loss of volatile components, or reversible phase changes such as crystalline transitions are all easily

* It had been discovered earlier (Bohan, 1961) that several new interfacial phases appeared at -35 to -50 C in certain particulate systems containing water.

detectable by DTA. In a low temperature DTA study of a solid rocket propellant one might expect to encounter such phenomena as the freezing out of one or more components, demixing of components, crystalline transitions in some components, and transitions from a plastic to a glassy state. A DTA study fixes the temperature or range of temperature at which such reactions occur, and from the results one is often able to deduce the cause of the reaction with reasonable certainty. However, investigation by other methods is usually required to identify the process positively. The principal purpose of a DTA investigation is to quickly discover the temperature ranges in which processes of interest occur. Once located, these temperature ranges can be investigated in detail to obtain additional information.

A search of the solid propellant literature produced a number of references to DTA studies of solid propellants and common propellant components but no reference to low temperature DTA studies. This is not surprising since low temperature DTA is a relatively new field and only a few organic compounds have been subjected so far to this kind of analysis. Most of the articles cited below deal with propellants or propellant components that have been studied at ambient and higher temperatures.

Brown and McLaren (1962) utilized DTA together with electrical conductance, optical microscopy, X-ray diffraction, and nuclear magnetic resonance measurements to study the thermal transitions in solid ammonium nitrate. Transitions among five stable crystalline forms of ammonium nitrate were known to exist and a metastable transition had been observed but not explained. They placed the sample in a glass tube which in turn was fitted into a brass block. Iron constantan thermocouples measured the sample temperature T and the difference ΔT between the sample and the block. The block was placed in a loosely fitted glass tube, wrapped with heating tape to raise the temperature, and cooled by replacing it in a similar tube immersed in a dry ice/acetone bath.

For undried samples of ammonium nitrate they found that the transition from IV to III occurred at about 37°C during heating. However, cycling the sample between 0 and 140°C resulted in IV to II transitions at 50°C without passing through form III. Transitions from III to II and II to I occurred at about 86°C and 126°C respectively. During cooling the transition from I to II occurred at 125°C, but the next transition was II to IV at 50°C and not II to III as was expected. Samples which had been heated to state II showed a II to III transition on cooling to 80°C and a III to IV change at 29°C. The investigation did not include the transitions to and from form V which are known to occur at about -18°C. Drying the sample under vacuum at room temperature and at 70°C did not affect the transition between forms III and IV, but cycling a sample between 0 and 60°C under a vacuum did eliminate the transition to form III. Optical examination of slowly grown crystals confirmed the transitions between forms IV and III in crystals with occluded mother liquor which, incidentally, produced severe cracking. Clear portions containing no occluded solution showed transitions between IV and II at about 50°C with only slight distortion. X-ray diffraction of non-occluding single crystals also showed no transition between IV and III. It was concluded that the severe cracking of crystals accompanying the transitions between III and IV allowed a sample to dry thoroughly during cycling; simple heating in a vacuum does not eliminate the occluded solution. A perfectly dry sample will show transition only between forms V, IV, II and I; the transitions between IV and III are due to dissolution and recrystallization phenomena. This study is important because ammonium nitrate is a convenient reference substance for DTA investigations and was so employed in the present work. A typical curve obtained with the apparatus employed in this investigation is given in Figure 1.

Kissinger and Newman (1962) reviewed the application of DTA for determining molecular structure in polymers. They stress that little work has been done on these substances; fewer than 12 reports were located in the literature prior to 1960. The report shows that DTA can be very useful in explaining reaction mechanisms in polymers. However, two annoying problems are pointed out. Most polymeric compounds have a low thermal conductance, which leads to large temperature gradients within a sample; and determining the temperatures of thermal events accurately is difficult

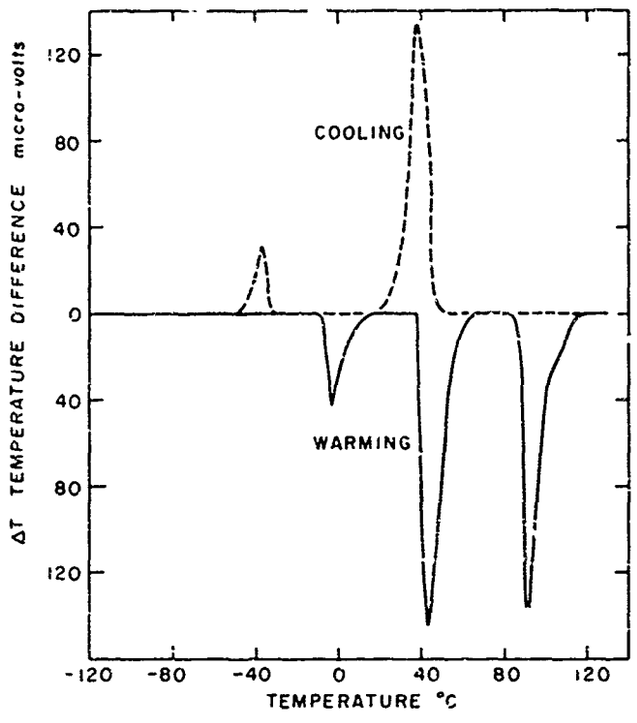

Figure 1. DTA curve of ammonium nitrate obtained during this study.

in such cases. The second problem involves removing the sample from the cell after a run. Many polymers and especially resins tend to adhere or chemically bond to the cell. Among the studies cited is that of White (1955) on the effect of mechanical deformation on melting behavior. Undrawn fibers of Nylon 6, 66, and 610, and certain copolyamides were melted giving a single endothermic peak. When the fibers were deformed by drawing, a second endotherm appeared before melting (Fig. 3), apparently due to the loss of preferred orientation. Polyethylene and Nylon II were unusual in that they did not show the extra peak when subjected to the same treatment. Also cited is the work of Ke (1960) in which the degree of crystallinity of polyethylenes was determined from the area of the melting peak. As expected, the less crystalline compounds produced the smaller heat effects on melting.

DTA has been used to determine the glass transition temperatures of polymers. Keavney and Eberlin (1960), for example, determined glass transition temperature as a function of molecular weight for polyacrylonitrile by this method. To answer a possible objection Murphy (1960) showed that heating rates ranging between 1 and 6°C per minute did not affect the measured glass transition temperature of polymethyl methacrylate or polystyrene appreciably and that the values determined by DTA agreed well with other methods.

Finally, attention is called to the work of Ayres and Bens (1961) who developed an apparatus for obtaining a continuous gas evolution profile along with DTA data. Comparing the two greatly aids in characterizing the DTA data. For example copious gas evolution normally does not accompany reactions such as simple fusion and crystalline transitions. Results obtained with a double-based propellant and its individual constituents are illustrated in Figures 2-5. The three main constituents of this formation (see Table 3) and their proportions were nearly the same as that of N-5. As Figures 2-5 illustrate, the thermogram and gas evolution profile of the propellant were not simple composites of the graphs which the individual constituents produced. Ethyl

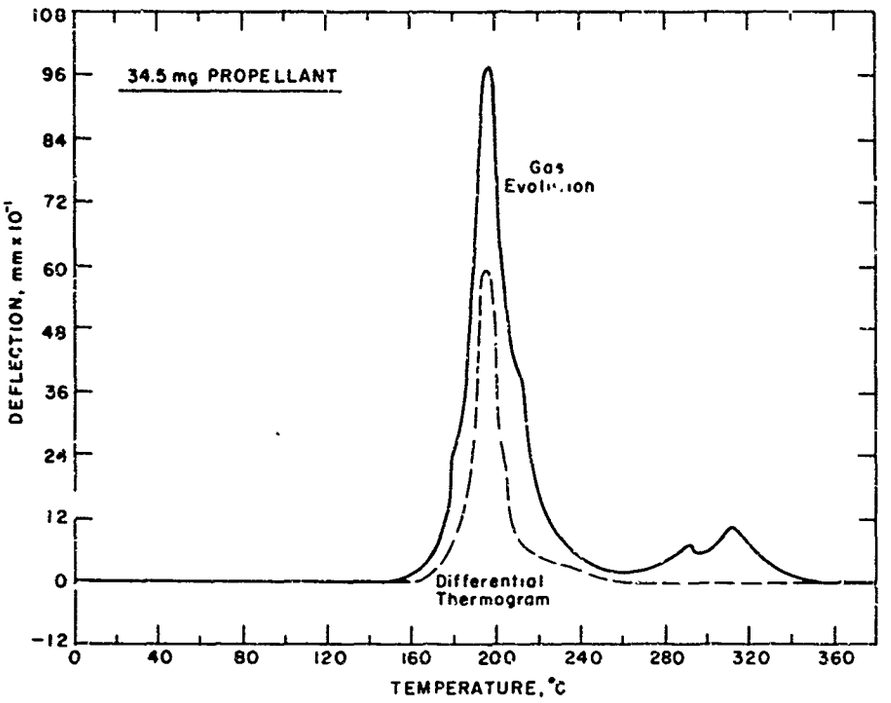

Figure 2. Analysis of double-based propellant by Ayers and Bens (1961).

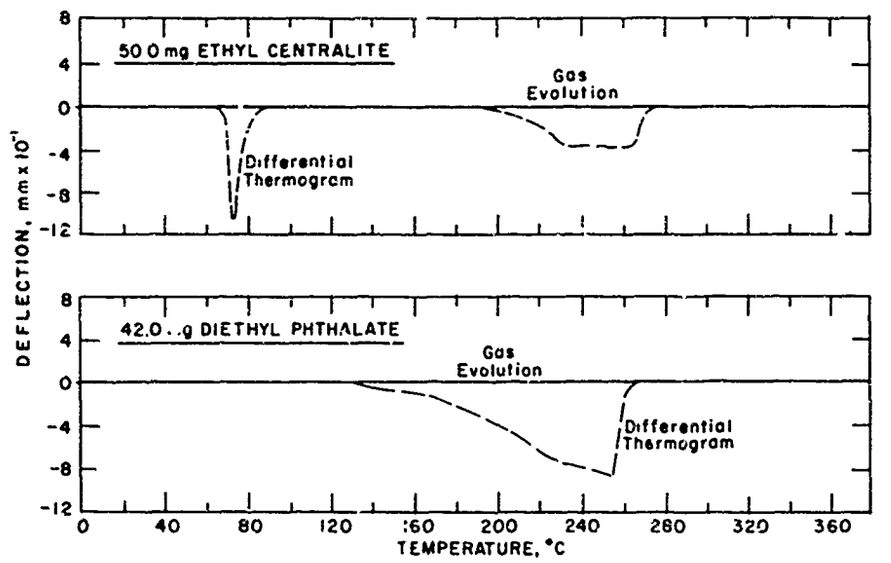

Figure 3. Analysis of constituents of double-based propellant by Ayers and Bens (1961).

centralite produced endotherms for fusion and vaporization as did diethyl phthalate also; but the vapors evolved evidently condensed in the exit tube for they did not reach the detector. Plastisol nitrocellulose produced an exothermic peak at 202°C, accompanied by a nearly identically shaped gas profile. The authors state that unplasticized nitrocellulose would produce a peak shifted to 190°C. The gas profile indicates that this is a decomposition reaction. Nitroglycerin produced an endotherm peaking at 191°C due to vaporization and some decomposition. The gas profile showed a maximum evolution at 202°C. At higher temperatures (about 240 to 350°C) the revaporization of

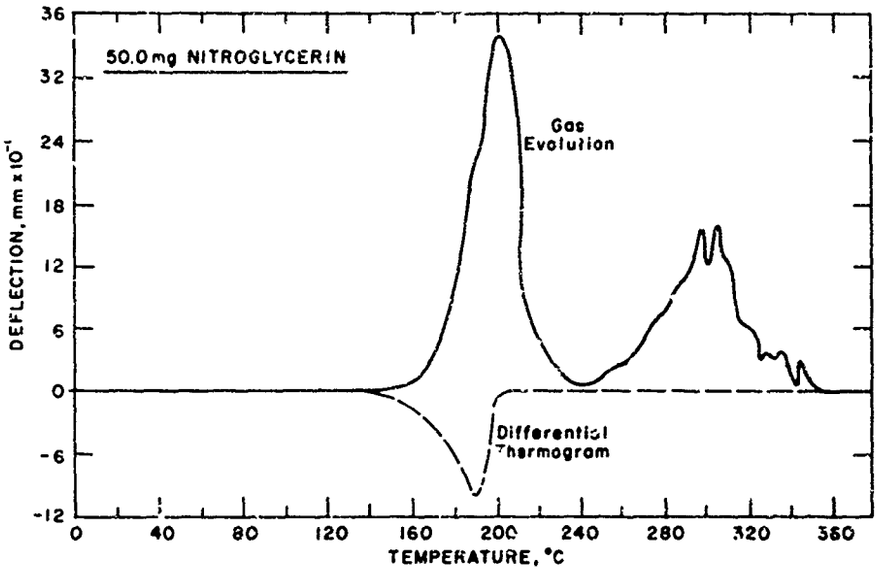

Figure 4. Analysis of constituents of double-based propellant by Ayers and Bens (1961).

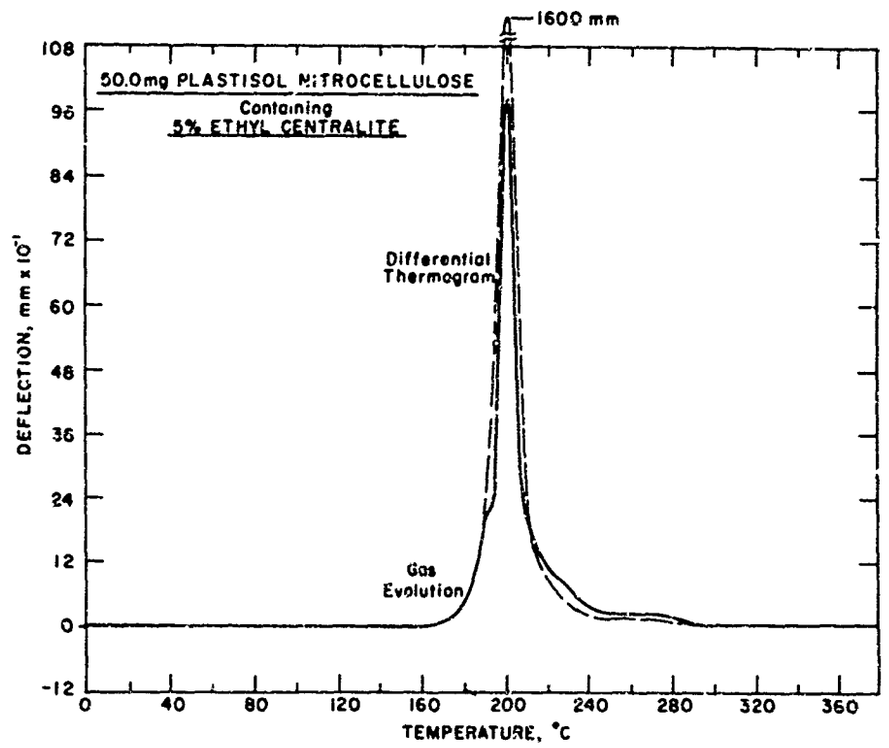

Figure 5. Analysis of constituents of double-based propellant by Ayers and Bens (1961).

portions previously condensed in the line leading to the detector produced spurious indications of gas evolution that was not evident on the DTA thermogram. Potassium sulfate and carbon black showed no reactions up to 500°C.

The DTA thermogram of the cured propellant showed no peaks corresponding to either ethyl centralite or diethyl phthalate. It was suggested that this may be due to the small amounts present or because of interactions among the constituents. An exothermic peak corresponding to the

Table I. Formulation of propellant studied by Ayers and Bens (1961).

Constituent	*Weight (%)*
Plastisol nitrocellulose*	50.00
Nitroglycerin	35.00
Ethyl centralite	2.63
Potassium sulfate	1.25
Carbon black	0.20
Diethyl phthalate	10.92

* 12.6% nitrogen

decomposition of nitrocellulose and distilled nitroglycerin occurred at 197°C. The difference in peak height of the propellant and the net peak heights of the constituents was reportedly due to sample size and possibly some interaction. The peaks above 270°C in the gas profile were attributed to partial decomposition of nitroglycerin which had condensed in the exit tube. A clear liquid which remained in the tube was identified as nitroglycerin and diethyl phthalate.

EXPERIMENTAL METHODS

Detection of phase changes

To prevent accidental ignition of the propellant grains during handling, aluminum sheeting 0.005 in. thick was layed upon the floor and all bench areas where the propellant samples were handled and was connected to the building electrical grounding system. Only non-sparking metals were used to cut the grains. Except for sample weighing, all operations were carried out under a forced draft chemical hood.

The DTA cell constructed for this work consisted of a metal cylinder 2 in. long and 1½ in. diam with a ½ × ½-in. diam hole milled into each end. Copper constantan thermocouples embedded in the sample and reference material provided the DTA signal and a record of sample temperatures. The reference end of the cell was covered with a 1½ × ½-in. metal end cap secured by machine screws. Thin aluminum foil was placed over the sample and a 1½ × ½-in. end cap with a ¼-in. hole drilled through the center was installed. The hole was filled with glass wool to provide thermal insulation. This construction provided for the easy escape of gases, if the ignition point of the propellant was accidentally exceeded.

Analyses were done with Al_2O_3, glass wool and glass beads serving as reference materials in successive runs. This procedure was followed because low temperature DTA studies are not numerous and the degree to which common reference materials react at low temperatures has not been established with complete reliability. In addition, we hoped to nearly match the thermal conductivity of the propellant in order to minimize base line drift. Of the three materials, Al_2O_3 met this requirement best; it is therefore taken as the reference material for this report. To further establish the reliability of the apparatus and method, the DTA curve of oven-dried NH_4NO_3 (Fig. 1) was observed periodically throughout the course of the work. This material undergoes several reversible phase changes within the temperature region of interest and was therefore used whenever calibration runs were desired.

With the samples and end caps in place, the cell was suspended over the surface of liquid nitrogen contained in a Dewar flask. A Styrofoam cover was placed over the flask to contain the nitrogen vapors. A constant speed stirrer was used to cool the sample. The sample was heated

by means of a resistance wire wrapped around the cell and controlled by a variable transformer. The cooling rate of the sample was from 2°C to 3°C/min, while the heating rate was normally about 10% faster.

Initially, to begin a run the samples were simply cooled from room temperature to about -120°C. Later, in order to standardize the procedure and to minimize the possibility that the prior thermal history of the propellant could influence the results significantly, the samples were quenched in liquid nitrogen, heated at a controlled rate to +120°C, then recooled at a controlled rate to -120°C. The heating and cooling pattern was repeated several times to study the reproducibility of the DTA signals and the effects of temperature cycling on the propellant.

Determination of T_g

The glass transition temperature (T_g) for polymeric systems is usually defined in terms of the volumetric or linear thermal expansion coefficient. It is the temperature at which a marked reduction of the thermal expansion coefficient from a value characteristic of a viscous liquid to one characteristic of a solid occurs. Frequently, the glass transition point is sharply defined and therefore easily located. In some cases, however, the glass transition occurs gradually over a large temperature range and more than one break in the thermal expansion plot may be observed. Since the density of an object depends on its volume, a graph of propellant density versus temperature is expected to consist of linear portions of different slopes which intersect at the transition temperature(s). This furnishes the basis for the first of two methods used here to determine T_g. The second method was a conventional measurement of the linear coefficient of expansion.

Initially the volumetric contraction with lowering temperature was studied by an improvised method and apparatus since we wished to make as rapid a determination as possible with the equipment at hand. A sample of propellant approximately 6 × 1.5 × 1 cm was suspended, by fine nichrome wire, from a Mettler balance in a 3.5-cm-diam glass tube containing about 8 in. of Dow 200 fluid. That portion of the tube which contained the fluid and sample was suspended, above the level of liquid nitrogen, in a Dewar flask. The mouth of the flask was closed with Styrofoam and the cold air was stirred at 600 rpm. The temperature of the Dow 200 fluid was monitored by a copper-constantan thermocouple placed near the sample and connected to a Moseley strip chart recorder. The weight of the immersed sample was recorded at regular temperature intervals down to about -70°C and a temperature vs weight graph was plotted.

Later, when time permitted, T_g was obtained by the conventional measurement of the linear expansion coefficient. A length of propellant was placed in a closely controlled refrigeration chamber and was cooled in progressive steps, allowing sufficient time for stabilization at each desired temperature. The linear contraction of a 10-in. section of the sample was measured optically, through a window in the chamber, by two parallel telescopes. The scopes were sighted in on two marks 10 in. apart on the sample at ambient temperature and the contraction was read off the calibration scale for the adjusting screw. The amount of contraction was then subtracted from the previous length and a temperature vs length graph plotted. The glass transition point and coefficients of linear expansion were also determined independently by Hercules Incorporated, Chemical Propulsion Division, Magna, Utah, at a later date. The work was done using a combination of ICRPG test method 4.9.1 and Bacchus Laboratory procedure, section III, method 88.

Determination of variability in propellant properties

To obtain an index of plant-to-plant variability in the physical properties of N-5, a sample consisting of five randomly chosen grains was taken from four different powder lots at each of the three plants currently producing this propellant. A tensile test sample was machined from each grain and strained at a crosshead speed of 2.0 in./min at a temperature of -65°F. To obtain an estimate of within-plant variability, propellant from the largest producer (Sunflower Army Ammunition

Plant) was subjected to tensile tests at four temperatures and two strain rates. This provided data that could be time-temperature shifted to give values at low equivalent strain rates down to -65°F. When treated in this manner the data yield the stress relaxation modulus needed in a propellant grain structural analysis.

Tensile tests were run according to Bacchus Laboratory procedure, section III, method 89. Twelve samples were tested at -65°F (-53.9°C), -40°F (-40°C), -15°F (-26.1°C), at crosshead speeds of 0.2 in./min and 20 in./min. In addition a group of 12 samples was tested at +77°F under 1000 psi external pressure. A chemical analysis of composite samples from each of the four lots from the three plants was accomplished by standard methods.

Propellant density was measured according to Mil. Std. 286, Method 510.1.1.

Nitroglycerin was determined according to Mil. Std. 286, Method 208.1.3.

2 Nitrodiphenyl amino was determined according to Mil. Std. 286, Method 208.4.2.

Total lead was determined according to OD 17094.

Diethyl phthalate was determined according to Mil. Std. 286 Method T.222.1 but with solvent in place of CCl_4.

In addition, nitroglycerin was determined by two Hercules methods employing infrared spectrometry.

RESULTS

Detection of phase changes

In an interim report dated 8 April 1968 (Anderson, Tice and Sterrett), the results of 50 DTA analyses of extruded N-5 propellants were discussed. These analyses were performed on propellant from the Sunflower Army Amunition Plant's lot number 6886. Many of the initial analyses were concerned with determining operational procedures such as optimal heating and cooling rates, the effects of quenching in liquid nitrogen, and the effects of repeated temperature cycling. Samples were taken from various points along the length and circumference of the propellant grains. In nearly every case these analyses produced DTA curves like those shown in Figure 6. Subsequent research has made it apparent that a large percentage of the area under these curves is attributable to base line drift. This base line drift is due to the changing thermal conductivity of the propellant during heating or cooling. The problem was further compounded by the lack of a thermally inert reference substance with a heat capacity duplicating that of N-5. Fortunately, the onset of change from the glassy to the plastic state during the heating cycle is marked by a sharp change in heat capacity which is well defined in all the graphs. The opposite event on cooling (i.e. the completion of transition to the glassy state) was also detectable on some runs. The average T_g values, taken at the point of inflection, for Sunflower lot 6886 were -65°C on heating and -71°C on cooling. Hysteresis accounts for the difference in the two values.

Two samples from a lot 6886 propellant grain produced curves much different than those described above. As shown in Figure 7, these samples produced endotherms during cooling, at about 88, 55 and 20°C. The corresponding exotherms were observed when the sample was warmed. One of these samples was put through three temperature cycles, the other through two; also, two reference materials, glass beads and alumina, were tried. It seems clear, therefore, that the observed peaks are correctly attributed to the propellant. Unfortunately, both samples spontaneously ignited during attempts to extend the analysis to 120°C. Melting occurred at 105°C, a much lower temperature than observed with other samples tested. These two samples were clearly anomalous and are indicative of propellant grain inhomogeneity. The precise nature of the grain inhomogeneity, however, is unknown at the present time.

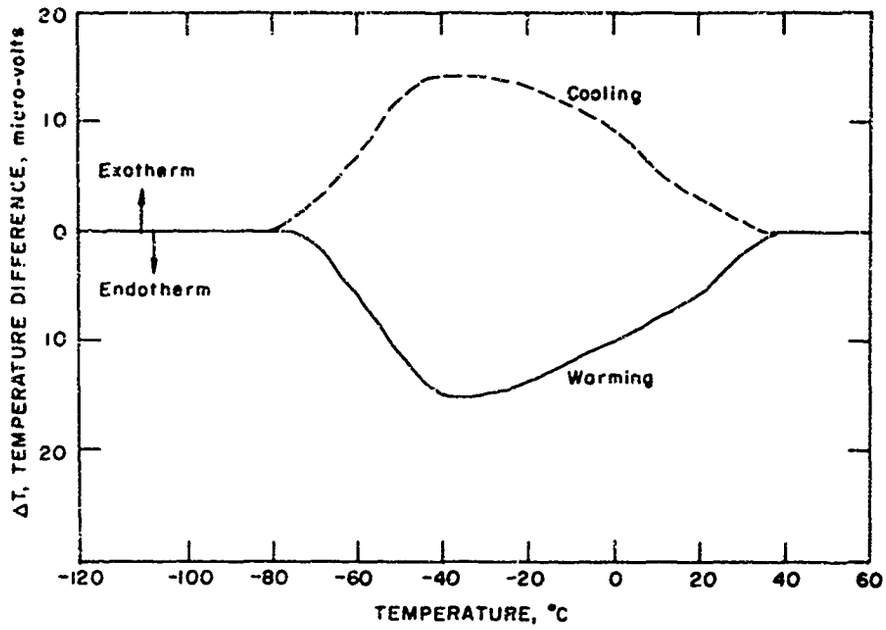

Figure 6. A typical thermogram of N-5 propellant from the Sunflower AAP.

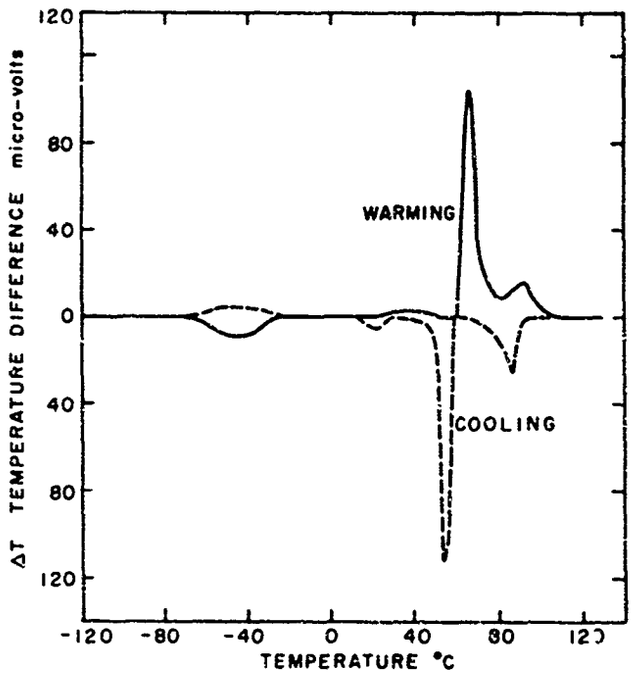

Figure 7. DTA curve of two samples from Sunflower lot 6886.

Meanwhile, 60 more DTA runs have been made, this time on samples from three different lots of propellant grains; two were produced at the Sunflower AAP and the third was extruded at the Naval Ordnance Station, Indian Head, Md. The number of heating and cooling cycles each sample was put through varied from two to five, depending on how well base line drift and other instrumental variables could be controlled and whether extra cycling was desired. On an average, each sample was quenched, put through two cycles, and warmed again to room temperature. Typical results are shown in Figures 8-11; these are reported in some detail in the following pages.

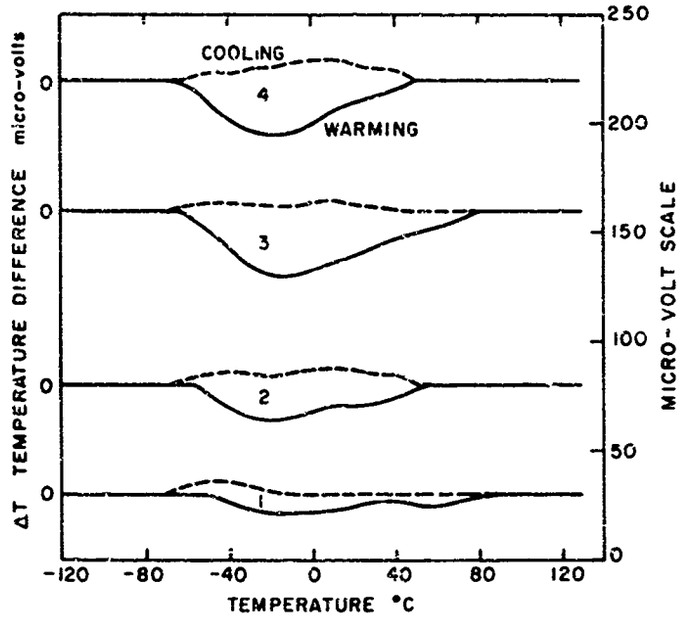

Figure 8. DTA curves of four samples from Sunflower lot 6943.

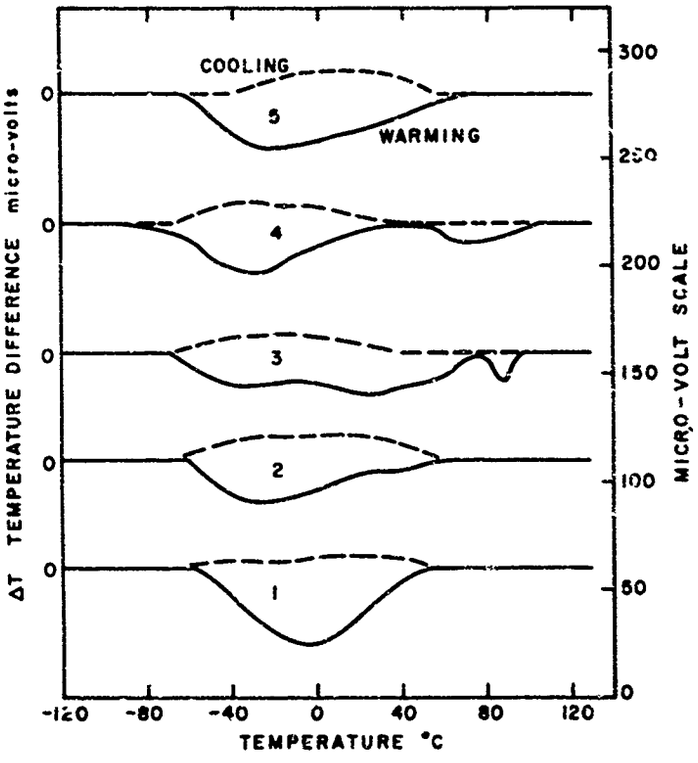

Figure 9. DTA curves of five samples from Sunflower lot 4872.

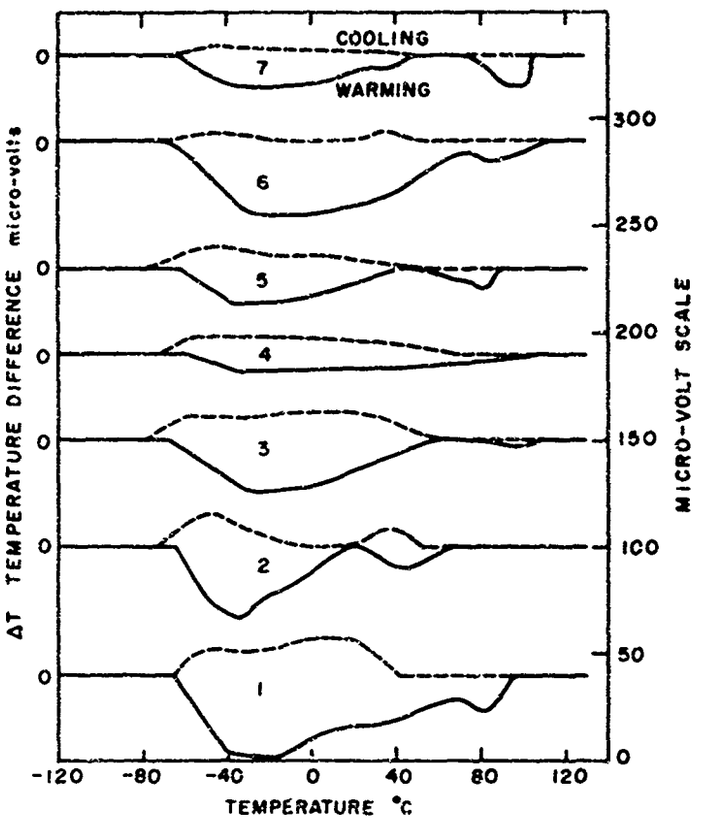

Figure 10. DTA curves for samples from Indian Head Naval Ordnance Station.

Four samples were taken from a grain of Sunflower propellant marked lot 6943. The sampling sites were spaced evenly over the length of the grain, beginning approximately 2 in. from either end, and were numbered forward from the nozzle end. Figure 8 shows representative traces for the analyses of each sample.

Five sample cores were taken from a grain of propellant produced in 1955 (lot 4872) by the Sunflower AAP. This lot was considered to be an example of satisfactory propellant and was run for comparison with the current production. The sampling sites were spaced as follows: 1 was three inches from the nozzle tip; 2 and 3 were five and ten inches forward of 1, respectively; 4 was eleven inches forward of 3; and 5 was centered between 3 and 4. As Figure 9 shows, all five samples produced traces on cooling which agreed well with those of later production lots. The traces of samples 1, 2 and 5 which appeared on heating were also very similar to those of later production lots, but samples 3 and 4 each produced an apparent endotherm in the upper temperature region during one of their cycles. During other cycles these two samples showed no such activity in that temperature range. In the case of sample 4 the second peak is very similar to an undulation in the endotherm produced by sample 1 of Sunflower lot 6943. An explanation for these exotherms is not at hand, but it may be that portions of the sample are hindered in the glass transition, or stresses incurred during cooling are suddenly released at higher temperatures.

The propellant received from Indian Head Naval Ordnance Station has been thoroughly analyzed since the interim report was written. Samples were taken within ½ in. of either end of the grain and at 2-in. increments. Thirty-eight runs were made on these samples, during which DTA

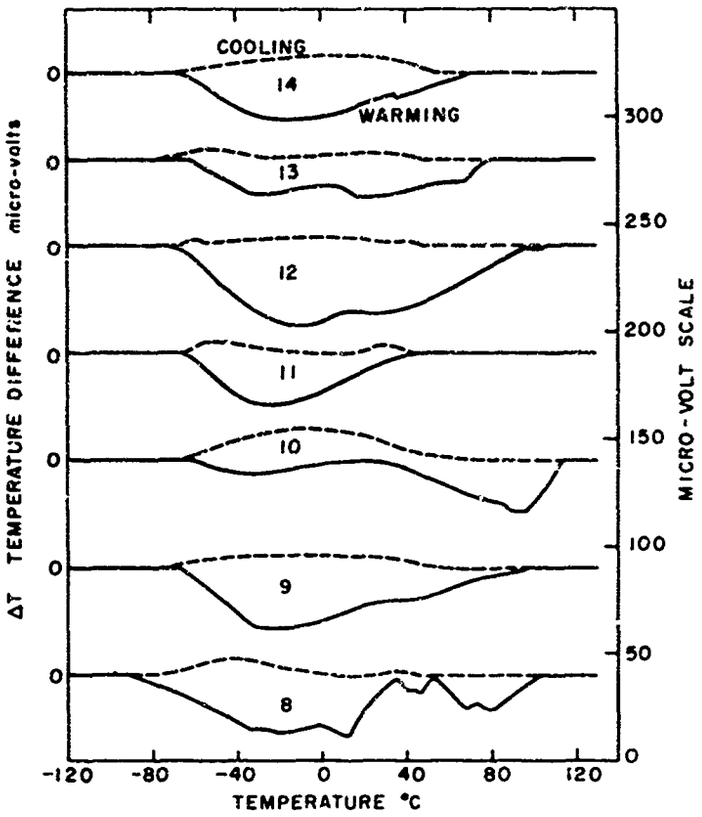

Figure 11. DTA curves for samples from Indian Head Naval Ordnance Station.

Table II. Average glass transition points by DTA.

Lot	T_g Heating (°C)	T_g Cooling (°C)
Sunflower lot 6886	-65	-72
Sunflower lot 6943	-62	-69
Sunflower lot 4872	-64	-72
Indian Head	-64	-71

curves were taken twice during cooling and three times during warming portions of the thermal cycle. Figures 10 and 11 show the representative DTA traces for the 14 samples. Half the samples produced a second peak at about 80°C during one of their cycles. In most cases, this peak occurred sporadically on one or two of the three temperature cycles. Two samples of Sunflower lot 4872 also produced a peak with this property, and the explanation advanced is that the second peaks result from the relief of nonreproducible stresses. Examination of the samples after they were removed from the DTA cell showed that sample 3 of Sunflower lot 4872 and samples 1, 3, 5, 7, and 13 of the Indian Head lot had developed visible cracks parallel to the hole drilled for the thermocouples. Each of these samples had produced an anomalous endotherm at about 80° C during warming. It may be that other samples which gave a peak at this temperature might also develop cracks upon further cycling. In any case, the correlation between the peak and the cracks seems quite convincing.

As reported in the beginning of this section, T_g was taken as either the inflection in the DTA trace due to the start of transition from the glassy to the plastic state on heating or the inflection due to the finish of the transition to the glassy state on cooling. Table II gives the average values of T_g for each propellant lot. The maximum deviation of individual values of T_g was ±5°C. Thus it can be said that within the limits of the experiment, all lots tested had the same glass transition point.

Summary (DTA)

All samples tested produced a DTA trace that is best attributed to the glass transition. No peaks indicative of demixing or sequential freezing of components were observed. In a few instances peaks were observed that appeared to be correlated with microscopic cracking of the propellant when it was cycled between -120 and +120°C. Of all the samples tested by DTA, only two showed appreciable abnormality. These occurred in one grain of lot 6886 and were shown in Figure 7. The sharpness of the anomalous peaks and their reproducibility suggest the presence of a substance other than N-5. This might be due to a separation of the grain components but is more likely to be attributed to imperfect mixing or the presence of an impurity. Of particular significance is the fact that these two samples melted at a much lower temperature than samples taken from the rest of the grain. Another observation worth noting was the splitting of one sample of Sunflower and six samples of Indian Head propellant during the analysis. In fact, the incidence of splitting was the only distinguishing difference found in the samples from the two plants. The cracking no doubt is due to stresses accumulated during the initial quenching and cycling to temperatures quite far below the propellant's working range. This is a manifestation of the well known embrittlement of N-5 at low temperatures.

Determination of the glass transformation temperature (T_g)

Figure 12 shows the weight change of three samples of Sunflower N-5 propellant as the sample and surrounding Dow Corning 200 fluid are cooled slowly. The fluid (viscosity: 1.0 centistoke at 25°C) increases in specific gravity linearly with decreasing temperature (Fig. 13). The increase in density of the fluid is greater than the increase in the propellant's density so that the weight of the propellant in the fluid is seen to decrease as the temperature is lowered. As the graphs show, samples 1 and 2 were similar. The rate of apparent weight loss with decreasing temperature increased twice during cooling. The discontinuities were at -25 and -52°C, and -27.5 and -53°C respectively.

Sample 3 resulted in only one discontinuity, at -38°C. The two discontinuities of samples 1 and 2 together with the preceding DTA curves suggest that the glass transition takes place gradually over the temperature range they span. The third sample went through the transition at a temperature which is nearly the mean of the two transition points of the first two. Later, the conventional method was used to confirm the glass transition point: it involved measuring the linear contraction of a 10-in. section of propellant as the temperature was dropped in steps. Figure 14 shows two discontinuities in the length vs temperature graph at -18°C and -45°C. Because this system allowed the sample to equilibrate at each temperature, the observed transition temperatures shifted to slightly higher values. Both determinations confirm that the glass transition of the N-5 propellant begins and ends within the temperatures of prominence in the DTA peaks and above the static firing temperature of -65°F or -54°C. A similar value, -47°C, was obtained from measurements made at the Hercules plant (Hercules Inc., Bacchus Works, Magna, Utah, letter report MISC/15/5-492, 13 November 1968). Because no data were taken above -21°C, they did not observe the small transition at -18°C. They give the coefficient of linear thermal expansion α above the transition point as 11.4×10^{-5} in./in./°C and below the transition point as 6.8×10^{-5} in./in./°C. We compute the coefficient of linear thermal expansion to be 16.8×10^{-5} in./in./°C from +20°C to -10°C, 14.0×10^{-5} in./in./°C from -20°C to -40°C, and finally 7.3×10^{-5} in./in./°C from -50°C to -60°C. All things considered, the agreement between the two investigations is very good.

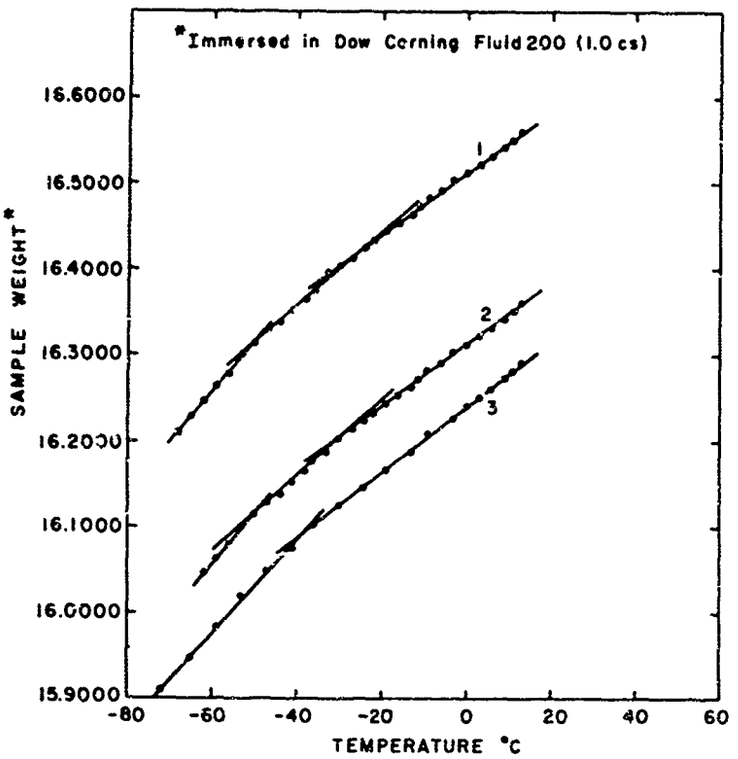

Figure 12. Apparent weight of propellant samples during cooling.

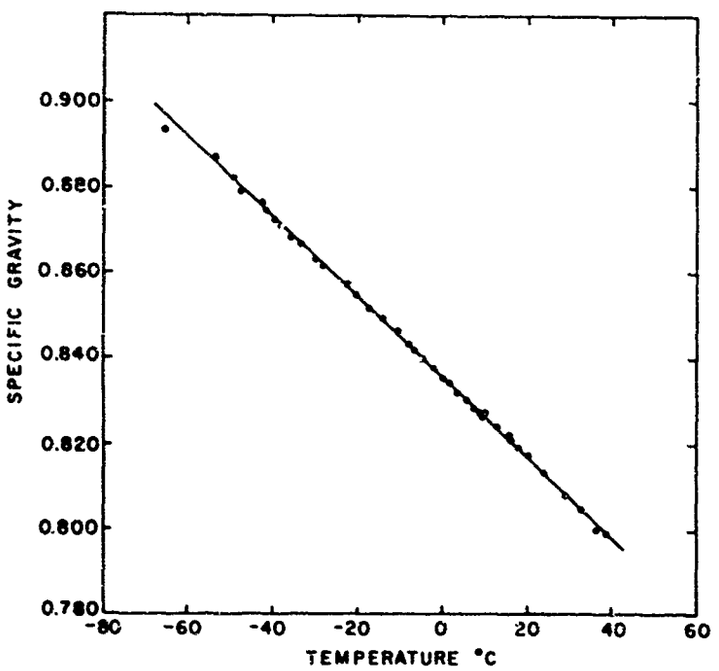

Figure 13. Dow Corning 200 fluid (1.0 cs).

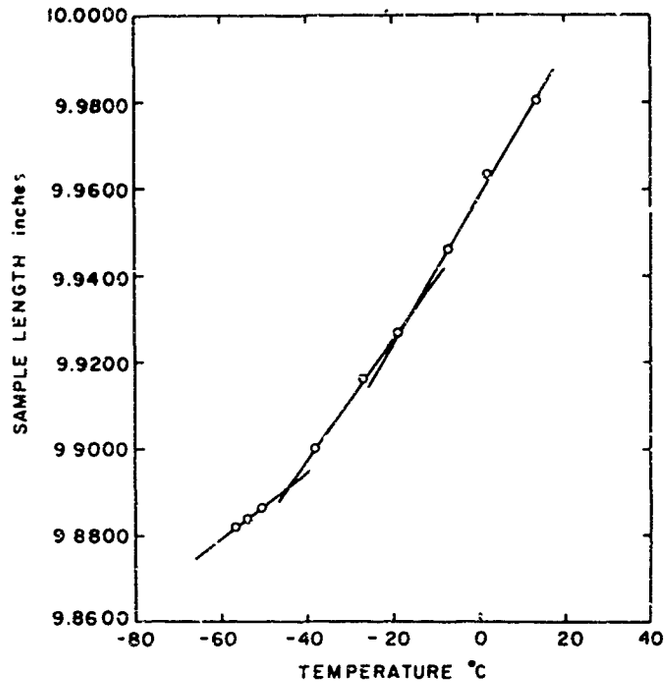

Figure 14. Propellant contraction during cooling.

It will be recalled that T_g for N-5 obtained by DTA was about -65°C; this is about 15°C lower than that determined by the methods described above. This situation is not without precedence. variations in T_g of this order are common and derive from differences in the rate of temperature change during the measurements and from a difference in the formal definitions of T_g inherent in the methods employed. Following the convention widely accepted in the field of propellant technology the value obtained by the methods described in this section is reported as T_g.

Converting our data to degrees Fahrenheit produces the following values:

Second order transition temperature, T_g: -58°F ± 3°F

Coefficient of linear thermal expansion α: from 68 to 14°F: 9.3×10^{-5} in./in./°F
-4 to -40°F: 7.8×10^{-5} in./in./°F
-58 to -76°F: 4.1×10^{-5} in./in./°F

Determination of variability in propellant properties

A comparison of some selected physical properties of N-5 propellant made by the three current producers is given in Tables III-VI. These data are contained in a Hercules Inc. letter report MISC/15/1-69, 2 October 1968. Examination of the data and the results of the analysis of variance shows that the average values of the three physical properties examined (tensile strength, elongation, strength modulus) were found not to vary significantly from plant to plant. A description of the calculations employed in the analysis of variance is contained in Table V. This analysis assumes a linear model of the form

$$X_{ijk} \quad \mu + a_i + \beta_{ij} + e_{ijk}.$$

The analysis of variance technique further assumes that the propellant samples are randomly chosen from normally distributed populations having approximately equal variances. Studies have shown

Table III. Table of means and standard deviations for each of the physical properties.

Each mean and standard deviation is based on five samples.

		Tensile strength (psi)		Elongation (%)		Modulus (psi)	
Plant	Lot number	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
Sunflower	6956	3,706	593	1.7	0.3	226,200	11,145
	6958	3,840	832	1.7	0.3	240,000	5,050
	6964	4,218	1,014	1.7	0.3	239,800	25,034
	6966	3,596	513	1.7	0.2	214,000	14,089
	All lots	3,840	741	1.7	0.3	230,000	18,111
Indian Head	2541	4,844	593	2.0	0.2	242,600	5,320
	2542	4,098	482	1.9	0.2	228,800	12,296
	2543	3,696	482	1.7	0.2	220,400	10,407
	2544	4,006	702	1.8	0.2	224,000	11,683
	All lots	4,161	680	1.8	0.2	228,950	12,808
Badger	7047	4,634	543	1.8	0.3	249,200	10 710
	7049	3,936	717	1.7	0.2	236,000	12,787
	7050	3,392	657	1.7	0.3	211,600	18,938
	7051	3,956	465	1.7	0.2	245,000	24,362
	All lots	3,980	715	1.7	0.3	235,450	21,972
All plants		3,994	713	1.7	0.3	231,467	17,950

that the results of the analysis of variance are changed very little by moderate violations of the above assumptions. Hence this analysis is considered reliable.

The analysis of variance shows, however, that there are significant variations in the physical properties of the propellant from lot to lot within each producing plant. For example, the maximum difference in the plant averages for tensile strength is 4,161 minus 3,840, or 321 psi (Table III). On the other hand, the maximum difference among lot averages within a plant for tensile strength is:

Sunflower	4218 − 3596 = 622 psi
Indian Head	4844 − 3696 = 1148 psi
Badger Army Ammunition Plant	4634 − 3392 = 1242 psi

The 321 psi is small in comparison to the 1148 psi and 1242 psi for the Indian Head and Badger lots.

One cannot, therefore, single out the product of one plant as being a great deal better than that of another. However it does appear (see Table III) that propellant from the Naval Ordnance Station at Indian Head had the lowest overall variation for all three physical properties. In statistical terms, the only variances that differ significantly among the plants is for strength modulus. Indian Head has a standard deviation of 12,808 psi which is considerably lower than 18,111 psi and 21,972 psi for Sunflower and Badger, respectively.

A structural analysis of the Mark 43 N-5 propellant grain was recently accomplished by the Dynamic Structures and Materials Analysis Group, Chemical Propulsion Division of Hercules, Inc. These results, contained in letter report MISC/6/40-1186, complete this investigation and may be

Table IV.

Pressure zero except as noted.

A – Specimen came from aft section.
B – Specimen failed at end of neckdown section at a point where radius starts, some shattering.
C – Specimen failed in neckdown center part.
D – Same as B except no shattering.
F – Specimen came from forward section.
T – Specimen failed in tab end and in radius; most of radius section shattered, many small fragments.

Plant	Lot	Crosshead speed (in./min)	Temp (°F)	Tensile strength (psi)	Elongation (%)	Modulus (psi)	Failure
Sun	6956-1		-65	4550	2.1	211,000	T
	2			3160	1.4	240,000	T
	3			4100	1.8	232,000	T
	4			3340	1.5	220,000	T
	5			3380	1.5	228,000	T
Sun	6958-1	2	-65	4180	1.9	245,000	T
	2			2800	1.3	236,000	T
	3			3130	1.5	236,000	T
	4			4350	1.8	237,000	T
	5			4740	2.0	246,000	T
Sun	6964-1	2	-65	2580	1.2	224,000	T
	2			4240	1.9	221,000	T
	3			4820	2.0	235,000	T
	4			4200	1.7	236,000	T
	5			5250	1.9	283,000	T
Sun	6966-1	2	-65	3590	1.7	203,000	T
	2			2780	1.4	200,000	T
	3			4120	1.8	233,000	T
	4			3560	1.5	224,000	T
	5			3930	1.9	210,000	T
Badg	7047-1	2	-65	5520	2.1	254,000	T
	2			4120	1.3	250,000	T
	3			4280	1.7	249,000	T
	4			4670	1.9	261,000	T
	5			4580	2.0	232,000	T
Badg	7049-1	2	-65	3350	1.5	223,000	T
	2			5130	2.0	256,000	T
	3			4060	1.9	224,000	T
	4			3520	1.5	239,000	T
	5			3620	1.6	235,000	T
Badg	7050-1	2	-65	4020	2.0	205,000	T
	2			2560	1.2	239,000	T
	3			3020	1.8	191,000	T
	4			4090	2.0	201,000	T
	5			3270	1.6	222,000	T
Badg	7051-1	2	-65	4440	1.7	274,000	T
	2			3660	1.5	253,000	T
	3			3380	1.7	210,000	T
	4			3890	1.5	255,000	T
	5			4410	1.9	233,000	T
IH	2541-1	2	-65	5100	2.1	241,000	T
	2			4540	1.9	237,000	T
	3			4070	1.7	239,000	T
	4			4860	2.0	246,000	T
	5			5650	2.3	250,000	T

Table IV (cont'd).

Plant	Lot	Crosshead speed (in./min)	Temp (°F)	Tensile strength (psi)	Elongation (%)	Modulus (psi)	Failure
IH	2542-1	2	-65	3710	1.7	233,000	T
	2			4440	1.9	245,000	T
	3			3540	1.8	215,000	T
	4			4690	2.1	218,000	T
	5			4110	1.8	232,000	T
IH	2543-1			3790	1.7	220,000	T
	2			4460	2.1	218,000	T
	3			3170	1.5	206,000	T
	4			3480	1.5	235,000	T
	5			3580	1.6	223,000	T
IH	2544-1	2	-65	3610	1.7	222,000	T
	2			3440	1.7	207,000	T
	3			4830	2.0	234,000	T
	4			4710	2.1	236,000	T
	5			3440	1.6	221,000	T
Sun	6956-1F	0.2	-15	3500	10.1	79,700	B
	4A			3440	10.6	79,700	B
	5F			3290	9.1	78,000	B
	6958-2F			3150	6.2	81,700	B
	3A			3210	9.9	79,300	B
	4F			3020	7.3	72,600	B
	6964-1A			3320	9.9	70,900	B
	4F			3280	9.1	74,200	B
	5A			3380	7.3	80,400	C
	6966-1A			3420	9.0	72,500	B
	2A			3220	7.9	81,300	B
	5F			3500	11.1	83,200	B
Sun	6956-1A	0.2	-40	3010	4.0	176,000	B
	4F			3530	2.7	133,000	B
	5A			3230	2.7	126,000	B
	6958-2A			5580	4.9	133,000	B
	3F			4280	3.6	119,000	B
	4A			2840	2.2	133,000	B
	6964-1A			2550	2.0	123,000	B
	4A			4800	4.0	123,000	C
	5F			4920	4.0	135,000	B
	6966-1F			4360	3.4	134,000	C
	2F			4000	2.8	157,000	B
	5A			4320	3.1	144,000	B
Sun	6956-1A	0.2	-65	3650	1.5	245,000	T
	4F			3170	1.4	244,000	T
	5F			3050	1.2	263,000	T
	6958-2A			3600	1.4	247,000	T
	3F			3730	1.6	243,000	T
	4A			3170	1.4	221,000	T
	6964-1F			3500	1.5	234,000	T
	4A			4230	1.9	222,000	T
	5F			4440	1.7	257,000	T
	6966-1F			2810	1.1	256,000	T
	2A			2530	1.0	232,000	T
	5F			2400	1.0	231,000	T

Table IV (cont'd).

Plant	Lot	Crosshead speed (in./min)	Temp (°F)	Tensile strength (psi)	Elongation (%)	Modulus (psi)	Failure
Sun	6956-1F*	20	77	991	29.1	14,400	D
	4A*			931	29.3	15,300	D
	5A*			934	29.4	14,300	D
	6958-2F*			972	27.1	13,300	D
	3A*			1041	27.5	15,500	D
	4F*			1119	29.3	15,500	D
	6964-1F*			985	27.8	14,100	D
	4A*			1016	26.3	14,400	D
	5F*			983	29.6	14,800	D
	6966-1F*			917	32.0	14,100	D
	2F*			994	22.7	16,400	D
	5A*			1021	27.8	15,400	D
Sun	6956-1F	20	77	864	22.8	17,200	D
	4F			1050	27.2	17,500	D
	5A						D
	6958-2F						C
	3A			911	27.0	13,400	D
	4A			971	25.4	16,900	D
	6964-1A			978	26.5	15,500	C
	4F			882	25.7	15,500	C
	5A			947	28.5	16,800	D
	6966-1A			855	26.0		D
	2A			930	28.0	16,000	D
	5F			1000	26.4	18,300	D
Sun	6956-1F	20	-15	3930	3.6	111,000	B
	4A			2720	2.5	108,000	B
	5F			4930	4.8	111,000	B
	6958-2A			4750	4.6	111,000	B
	3F			5110	5.0	117,000	B
	4F			5790	6.4	117,000	B
	6964-1F			4580	4.4	111,000	B
	4A			4490	4.1	116,000	B
	5A			5380	5.1	114,000	B
	6966-1A			5060	4.9	110,000	B
	2F			4360	4.0	111,000	B
	5A			4310	4.4	105,000	B
Sun	6958-1A	20	-40	3480	2.0	103,000	T
	4A			3340			
	5A			2630	1.7	161,000	T
	6958-2A						
	3F			2680	1.5	182,000	T
	4A			4520	2.5	180,000	T
	6964-1F			3010	1.7	179,000	T
	4F			2810	1.7	167,000	T
	5A			3650	1.9	191,000	T
	1F			2440	1.6	159,000	T
	2F			3190	1.8	179,000	T
	5A			4300	2.2	189,000	T
Sun	6956-1A	20	-65	3070	1.2	258,000	T
	4F			2400	1.0	216,000	T
	5F			3780	1.4	268,000	T

* Pressure 1000 psi.

Table IV (cont'd).

Plant	Lot	Crosshead speed (in./min)	Temp (°F)	Tensile strength (psi)	Elong-ation (%)	Modulus (psi)	Fail-ure
Sun	6958-2F	20	-65	2140	1.7	183,000	T
	3A			2520			
	4F			3110	1.2	250,000	T
	6964-1A			2650	1.0	249,000	T
	4F			3440	1.3	252,000	T
	5F			2550	1.0	258,000	T
	6986-1A			1120	0.8	141,000	T
	2A			4410	1.5	286,000	T
	5F			2720	1.1	253,000	T

Table V.

Source of variation	Degrees of freedom	Mean square	F-ratio	Level of significance
Tensile				
Among plants	2	518,145	0.55	NS
Among lots within plants	9	948,364	2.23	0.95
Among samples within lots within plants	48	42 ,140		
Total	59	506,111		
Elongation				
Among plants	2	0.126000	1.91	NS
Among lots within plants	9	0.0 111	0.56	NS
Among samples within lots within plants	48	0.065916		
Total	59	0.063559		
Modulus				
Among plants	2	243,517,000	0.27	NS
Among lots within plants	9	888,789,000	4.05	0.999
Among samples within lots within plants	48	219,225,000		
Total	59	322,185,000		

summarized as follows. When internal pressure loading is analyzed, the greatest strain is found to be a tensile radial strain at the slot tips. Analysis showed the minimum margins of safety for this loading to be 5.01 and 3.44 at 77°F and -65°F, respectively. When acceleration loading was considered, it appeared that the maximum principal strains were located in the aft end of the grain but they were very low, having a margin of safety of more than 500. The tensile hoop strain caused when the grain is cooled to -65°F in three hours results in a margin of safety of 1.16; but since the strains for thermal shrinkage loading are opposite the internal pressure loading strain, the combined strain loading situation results in a more favorable margin of safety than that resulting from either loading by itself. As a result motor failure is not predicted for static firing or flight conditions.

Table VI.

	Lot	Plant	Density[1]	NG[2]	2NDPA[3]	Total load[4]	NG[5]	NG[6]	DEP[7]
Badg	7047	BAAP	1.559 g/cm³	34.60%	1.97%	1.06%	34.70%	49.62%	10.62%
	7049		1.558	34.68	2.01	1.09	34.86	50.24	10.70
	7050		1.560	34.58	2.02	1.10	34.40	51.12	10.40
	7051		1.558	34.52	2.00	1.10	35.01	50.22	10.93
IH	2541	NOS	1.554 g/cm³	35.14	1.98%	1.12%	35.03%	50.56%	10.82%
	2542		1.556	35.82	2.02	1.10	35.59	49.88	10.94
	2543		1.556	35.44	2.04	1.11	35.40	49.74	10.92
	2544		1.556	36.00	1.96	1.08	35.17	49.74	10.66
Sun	6956	SAAP	1.562 g/cm³	33.94%	1.94%	1.24%	34.96%	51.24%	10.58%
	6958		1.558	33.93	2.01	1.14	34.55	51.92	10.52
	6964		1.561	34.64	2.01	1.15	34.82	51.69	10.84
	6966		1.558	34.42	2.09	1.16	34.40	51.72	10.68

1. Mil Std 286, Method 510.1.1
2. Mil Std 286, Method 208.1.3.
3. Mil Std 286, Method 213.4.2.
4. OD 17094.
5. Infra-Red-Hercules Method HD-CP-3027.
6. Infra-Red-Hercules Method.
7. Mil Std 286 T222.1 – solvent in place of carbon tetrachloride.

except that since shock and vibration loads induced by the motor itself could not be included in the analysis it cannot be concluded that the grain is completely adequate in a structural sense at low temperatures when N-5 propellant becomes very brittle.

SUMMARY AND CONCLUSIONS

The detailed differential thermal analysis of N-5 propellant shows no evidence of demixing or sequential freezing of its components, except in two anomalous instances. From this it is concluded that in general the propellant is well colloided and otherwise prepared during manufacture.

Lapses in quality control may sometimes occur leading to grain defects such as that thought to be involved in explaining the anomalous results of Figure 7. To repeat a truism, quality control at all stages in grain production is of the utmost importance. DTA revealed that the glass transition in N-5 is gradual and progressive down to about -60°F. Discontinuities in the thermal contraction curves were observed at about -20 to -25°C and at about -50°C. This agrees with the DTA observations indicating progressive embrittlement down to -60°C. The coefficient of linear thermal expansion was computed to be 16.8×10^{-5} in./in./°C from +20°C to -10°C; 14.0×10^{-5} in./in./°C from -20°C to -40°C; and, finally, 7.3×10^{-5} in./in./°C from -50°C to below -60°C.

An analysis of within-plant and plant-to plant variability in tensile strength, elongation and strength modulus of N-5 propellant showed significant differences between lots within a given plant but no significant differences between plants. A structural analysis of the Mark 43 N-5 propellant grain showed that motor failure is not predicted for either static firing or flight firing assuming a perfect, undamaged grain. Shock and vibration loading could not be included in the analysis however; hence it cannot be concluded that the grain is completely adequate, in a structural sense, at low temperatures where N-5 propellant becomes very brittle.

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13. ABSTRACT

The low temperature behavior of several samples of N-5 rocket propellant was studied using DTA. The only significant occurrence during cooling to -100°C was the glass transition. The temperature of this transformation was found to be -58°F ± 3°F by dilatometry. In addition, the variability of tensile strength, elongation, and strength modulus among three producers was examined. Significant variations were found among lots from any one plant; but variations in the average values for each plant were not significant.

14. KEY WORDS

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